

"On the Results of Chilling Copper-Tin Alloys." By C. T. HEYCOCK, F.R.S., and F. H. NEVILLE, F.R.S. Received February 12,—Read February 28, 1901.

(PLATES 2-3.)

In the Third Report of the Alloys Research Committee, published in 1895, Sir W. Roberts-Austen gives an appendix, by Dr. Stansfield, containing an extremely interesting series of cooling curves of the copper-tin alloys. These curves made it evident that for many percentage compositions there were three or even four halts in the cooling due to separate evolutions of heat, and that some of these changes must have occurred when the metal was solid. A freezing-point curve was also deduced from the cooling curves. The report contained interesting remarks on the meaning of the curves, but a satisfactory explanation was not at that time possible. In June, 1895, Professor H. Le Chatelier also published a freezing-point curve, giving the upper points only. These two curves agree in locating a singular point near the composition  $\text{Cu}_4\text{Sn}$ , but do not give any singular point nearer to the copper end of the curve.

In 1897 we also gave, in the 'Philosophical Transactions,' a freezing-point curve of these alloys. This curve was inferior to Dr. Stansfield's, inasmuch as it gave no information concerning the changes that go on in the solid metal, but it was a more accurate statement of the upper freezing points than had been given before. In particular, it pointed out a new singular point at 15.5 atomic per cents. of tin, the point marked C in the figure (fig. 1), and a straight branch of the curve joining C to the other singular point marked D in the figure. Both C and D are the origins of rows of second isothermal freezing points, better called transformation points. Like Dr. Stansfield, we found it impossible to offer a satisfactory explanation to the curve, but we hazarded the surmise that the steepness of the branch ABC might be due to chemical combination, and that in the region CDE solid solutions existed. Both of these surmises have since been confirmed, but at that time we felt no certainty on the subject.

In their report on alloys presented to the Congrès International de Physique in 1900, Sir W. Roberts-Austen and Dr. Stansfield give a curve embodying all the above-mentioned details and some others, in particular a most important lower curve of changes that take place in the solid alloys.\*

\* Our attention has been called to the fact that the copper-tin curve given by Roberts-Austen and Stansfield in the International Report on Physics in 1900 had already been published by them in the Fourth Report to the Alloys Research Committee in 1897. This correction does not alter the chronological sequence as stated in the text, since our paper was read before the Royal Society in June 1896.

It may be remarked that the freezing-point curve forms a useful chart to the general character of the alloys. For example, alloys whose composition lies in the region AB of the figure are red bronzes and gun metals, tough, but not very hard, while as we approach C the alloys become paler in colour and much harder. Alloys a little to the left of C are nearly white and extremely tough and strong; they are ideal bell metals. The moment we pass C the alloys begin to become brittle, and the brittleness becomes very great near D. The alloys between C and D are steel coloured; they have a glass-like

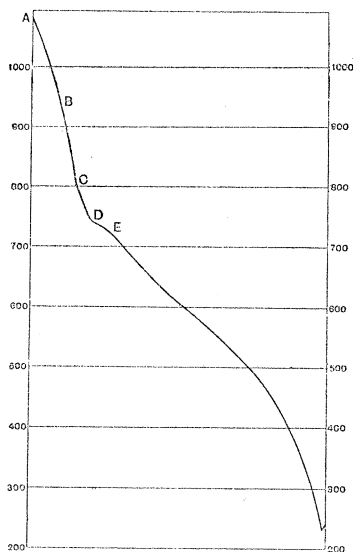


FIG. 1.—Freezing-point curve of the copper-tin alloys. Atomic percentages of tin are reckoned from 0 per cent. on left to 100 per cent. on right of diagram. (Extracted from 'Phil. Trans.,' A, vol 189, p. 63.)

hardness and take a fine polish; they are speculum metals, Lord Rosse's being the alloy at D. With more tin than that present at the point D the alloys deteriorate from a mechanical point of view, and except as anti-friction metals are not much used.

In 1900 we commenced a study of these alloys by means of the microscope. As regards the regions ABC and that to the right of E we at first did little more than confirm results which we found had been already published both by Mr. Stead and by M. Charpy; but in the region CDE we appear to have observed more detail than is contained in the published work of these observers. We were especially struck by a discrepancy, in the region CD, between the crystals on the outside of the alloys and the internal pattern. Our habit was to

make the alloys in an atmosphere of coal-gas or hydrogen, and to allow them to cool in this atmosphere. If made in this way, we found that all alloys, from A almost to D, showed on the top of the ingot a regular crystallisation in relief, of the rectangular comb-like character so often seen on the surface of cast metal. This was as perfect in the white metals between C and D as in the red alloys between A and B. These crystals disappear when the point D is reached, although with much more tin other types of raised crystals are seen. These combs are of course primary crystals, standing out on account of the contraction of the solidifying mass and the consequent retirement of the mother liquid. When the ingots of alloy are cut, the surfaces polished, and the internal pattern brought out by ignition or etching, one sees, as Charpy and Stead have shown, that similar combs, rich in copper, occur in the interior of the ABC alloys, the combs being embedded in a matrix which is itself complex (see photo. 1, Pl. 2). These combs are numerous and large in the gun-metals of the region AB, but decrease in numbers, size, and perfection as we approach C. For some distance to the left of C they are much broken and distorted, and to the right of C they do not appear at all in the body of the alloys; but they exist on the outside in the same perfection as before. Moreover, if the top of one of the alloys anywhere between a point a little to the left of C and the point D be slightly ground down so as to obtain sections half through the raised crystals, and the pattern examined, it is found that the crystals are not homogeneous, as one would expect a crystal to be, but that each crystal is full of a well-marked pattern identical with that of the body of the alloy. To illustrate this peculiarity, we give a photograph of the top of the alloy containing 14 atomic per cents. of tin (photo. 2). Hence it appeared that the alloys underwent remarkable changes both during and after solidification. In the alloy of photograph (2) the larger detail in the substance of the bars of raised crystal, or something not unlike it, was formed before the raised pattern, but the smaller detail, hardly seen at this magnification, is more recent than the raised pattern.

Photograph (1) shows the large primary combs existing in the interior of an alloy containing 12 atomic per cents. of tin, and photograph (3) shows the utterly different pattern existing on the other side of C. It is that of an alloy containing 16.7 atomic per cents. of tin. It must be remembered that on the outside the alloy still shows the combs. These alloys were slowly cooled, that is, not subjected to any sudden chill during cooling. A pattern like that of photograph (3) is given by Charpy for an alloy containing equal weights of copper and zinc. We have also found it in some silver-zinc alloys, and we think it always means that changes have taken place in the solid alloy.

The patterns at all points on the curve were so puzzling that we

almost despaired of being able to interpret them, until after reading Professor Roozeboom's paper on the "Solidification of Mixed Crystals of Two Bodies," published in the 'Zeitschrift für Physikalische Chemie' of December, 1899. The beautiful theory contained in this paper made the attempt to decipher the hieroglyphic of the copper-tin alloys more promising; but the experimental method recommended by Roozeboom, that of isolating the first crystals that form when a liquid begins to solidify, is beset with almost insuperable difficulties in the case of metals melting at high temperatures. Cooling curves will, it is true, give the approximate moment of complete solidification of an alloy, and enable us to plot in a rough way the "solidus" curve, as Roozeboom calls it; but the solidus curve thus obtained is not nearly so accurate as the "liquidus" or freezing-point curve. We therefore had recourse to the microscopic examination of chilled alloys, a method which has thrown so much light on the nature of steel.

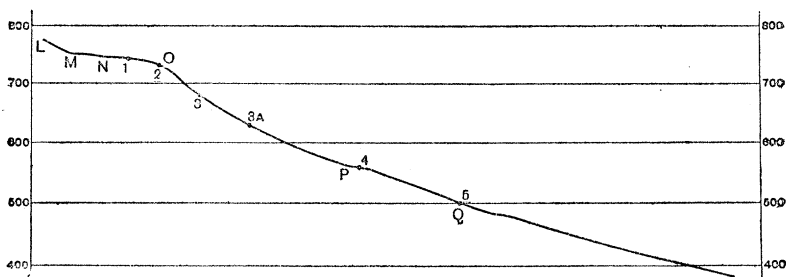


FIG. 2.—Cooling curve of the alloy  $\text{Cu}_{81}\text{Sn}_{19}$ . Percentages by weight: Cu 69.56, Sn 30.44. Time is measured horizontally. Equal vertical distances correspond to equal differences in platinum temperatures. The numbers at sides of diagram give temperatures on the Centigrade scale. The numbers on the curve are the points of chilling.

The first step was to imitate Austen and Stansfield and obtain a cooling curve of an alloy by means of a recording instrument. We used a Callendar recorder in connection with a platinum pyrometer. Fig. 2 is a small scale reproduction of the cooling curve thus obtained in the case of an alloy containing 19 atomic per cents. of tin. In this curve the temperature of the cooling alloy is measured vertically, and the time is measured horizontally. It will be seen that evolutions of heat occur during the period MNO and also at P and Q. Below the temperature O the alloy was a rigid mass, a solid. The temperatures marked 1, 2, 3, 3A, 4, 5 on the curve were then selected as points at which it seemed well to chill portions of the alloy. The pyrometer was therefore transferred to a bath of molten tin, heated well above the highest freezing-point of the alloy, and small amounts

of from 5 to 10 grammes of the alloy, contained in little test-tubes of Jena glass, were immersed in the bath; these were in an atmosphere of coal-gas, and so did not oxidise. The bath of tin was then allowed to cool slowly and uniformly, and when the temperature fell to one of the selected points, a tube was taken out and plunged into water. The alloy was thus chilled, the slow cooling being brought to an abrupt end at any desired temperature.

The chilled alloys were afterwards ground down and polished in the usual way. After the trial of many reagents for bringing out pattern, we adopted the method of slightly heating the surface until the film of oxide formed was of a pale yellow colour. Behrens some years ago recommended this method, and Mr. Stead has pointed out that it develops differences of chemical composition very well, while etching reagents complicate the picture by revealing the orientation of crystals and other details which are not always needed. With one or two doubtful exceptions, we find that in alloys richer in copper than  $\text{Cu}_3\text{Sn}$ , the parts which oxidise most rapidly, and are therefore darkest in the yellow stage, are the softer parts containing most copper. When alloys on the branch ABC are oxidised the pattern is very distinct to the eye, but it is sometimes difficult to obtain much contrast in the photographs; in such cases (for example, in the alloy of photograph 1) we etched the surface with strong ammonia, which also darkens the parts richest in copper. Alloys on the branch ABC are very sensitive to reagents such as ammonia or hydrochloric acid, and from C to D, where these have but little action, a mixture of hydrochloric acid and potassium chlorate etches rapidly. One can use these reagents to control the effect of heat oxidation in cases where the low temperature of chilling makes it possible that the heating needed to produce the yellow colour may have reversed the result of chilling; but we find that there is not much danger of such a reversal.

The upper point alloy, chilled at the commencement of solidification, was generally found to be granulated by the operation of dropping into water, but portions could always be found suitable for polishing; the other alloys had always solidified before the chilling, and therefore gave compact ingots.

After polishing, the alloys were heated until a pale yellow oxidation colour was produced on the surface.

Alloy (1), chilled when much of the metal was still liquid, shows a pattern of large primary skeletons, more or less comb-like in appearance, which oxidise much more rapidly than the mother substance, and which therefore contain more copper than it (photo. 4).

Alloy (2), chilled when the solidification was almost complete, shows skeletons much softer in outline and not differing much in oxidation colour from the ground; but these skeletons occupy a much larger

area than in (1), nearly filling the field, and being only separated from each other by an imperfect network of less oxidised mother substance.

These two alloys are deeply etched in the process of polishing with rouge, the softer primaries rich in copper being eaten away. The pattern is so large that it is best examined with a power of 10 or 20 diameters.

In striking contrast to the above, alloys (3) and (3) A, chilled when the alloy has been solid some time, show no pattern even with a power of 300 or 400 diameters (photo. 5).

Alloy (4), chilled at P, the next point of heat evolution on the cooling curve, shows a pattern which is a close approximation to that of a slowly cooled alloy, and alloy (5), chilled at a still lower temperature, is an almost perfect reproduction of the slow-cooled pattern (photo. 6). It will be noticed, however, that a little below the chilling point of (5) there is another stage of heat evolution, and in harmony with this we can find one point of difference between the pattern of (5) and that of the slowly cooled alloys of the region CD. Both in these and in (5) the surface is divided into large polygons bounded by bands of a smooth material, and the interior of each polygon is more or less full of a broken fern or flower-like crystallisation of the same smooth body as that of the bands. The ground in which the fern leaf lies is more easily oxidised than the material of the fern leaf and bands, so that the ground probably has more copper in it. In the slowly cooled alloys near C there is very little of the fern leaf, but as we approach D it increases in amount until at D it almost fills the whole area, not absolutely, however, for a network of the darker ground can still be traced here and there. A comparison of photos 3 and 6 illustrates this growth of the fern leaf with the increase in the percentage of tin. In the slow-cooled alloys the ground is granular—in fact, an immersion lens defines it as a well-marked eutectic. In (5), on the contrary, the ground appears to be uniform; probably chilling at a temperature below Q would convert it into the eutectic.

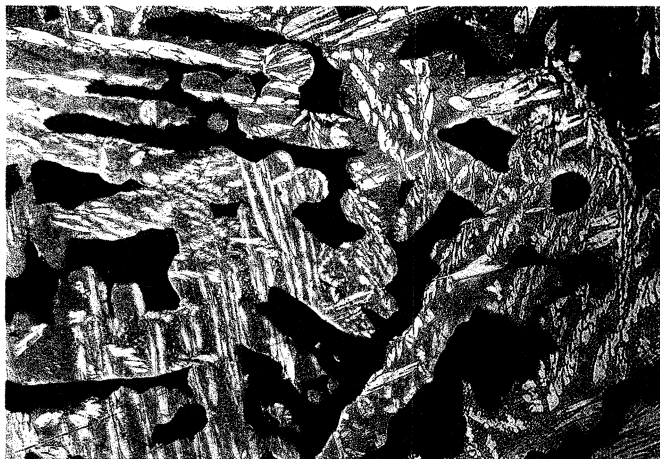
All the alloys from a little to the left of C to beyond D exhibit similar contrasts between the chilled and slow-cooled patterns, there being for each alloy a region of temperature such that if it be chilled in this region it shows no pattern. Alloys between D and E are still more remarkable when chilled.

If we apply Roozeboom's theory to these results, we see that in the cooling curve the branch LM corresponds, as is obvious, to the cooling of a liquid, and the short branch MN to the formation of mixed crystals separating out of a liquid that is continually growing richer in tin, so that the crystals are suffering transformation. The branch NO, almost flat at first, and then only slightly sloping, corresponds to an isothermal transformation of the mixed crystals followed by

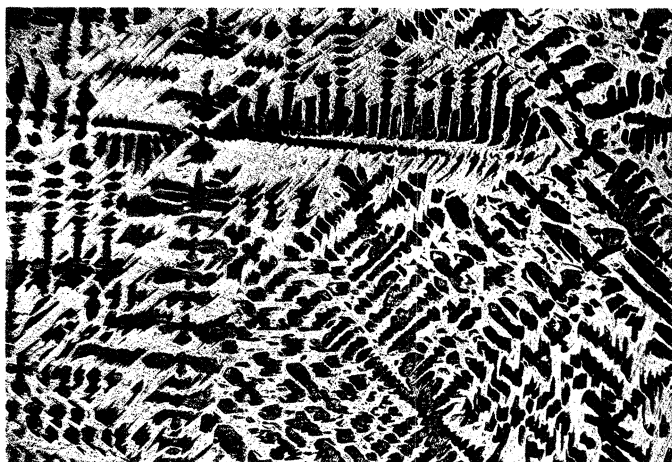
## DESCRIPTION OF PLATE 2.

Slowly cooled alloys.

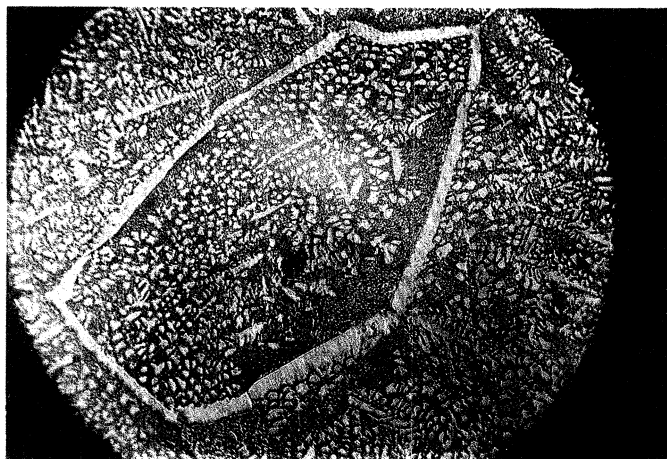
Formula.	Percentage by weight.	Magnification.	Treatment.
1. $\text{Cu}_{88}\text{Sn}_{12}$	$\begin{cases} \text{Cu} = 79\cdot7. \\ \text{Sn} = 20\cdot3. \end{cases}$	50 diameters.	Ammonia etch.
2. $\text{Cu}_{86}\text{Sn}_{14}$	$\begin{cases} \text{Cu} = 76\cdot7. \\ \text{Sn} = 23\cdot3. \end{cases}$	50     „	Heat-oxidised.
3. $\text{Cu}_{83\cdot3}\text{Sn}_{16\cdot7}$	$\begin{cases} \text{Cu} = 72\cdot8. \\ \text{Sn} = 27\cdot2. \end{cases}$	300     „	„     „



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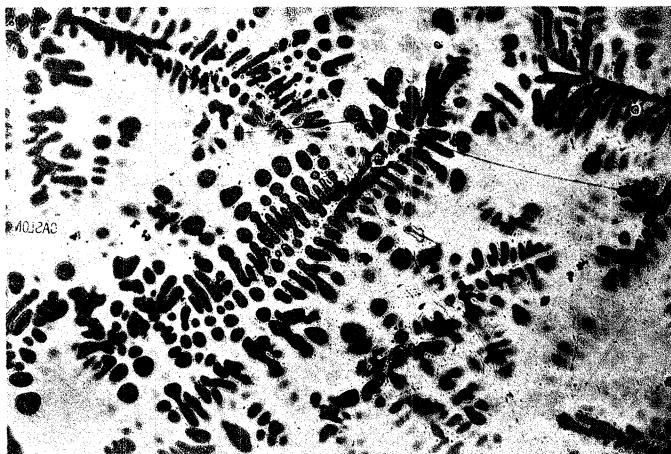
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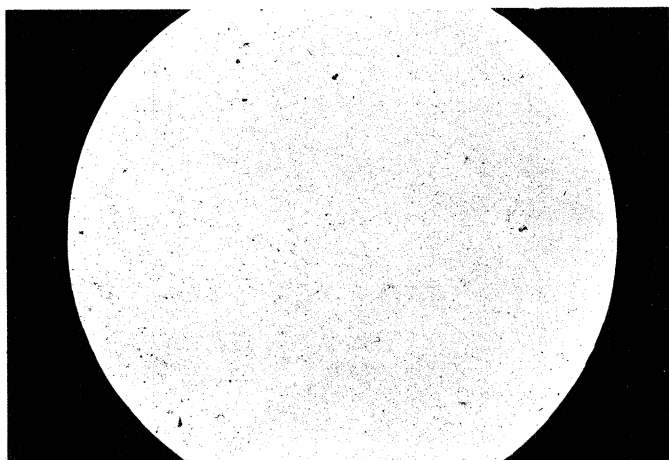
# DESCRIPTION OF PLATE 3.

The same alloy chilled at different temperatures.

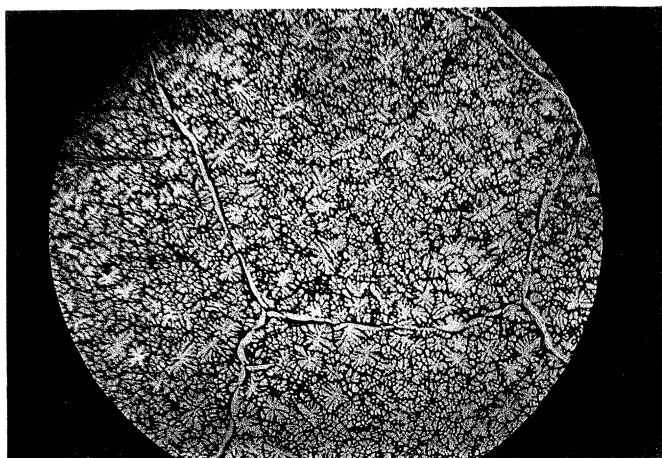
	Formula	Percentage by weight.		Magnification.	Treatment.
4.	$\text{Cu}_{81}\text{Sn}_{19}$	$\left\{ \begin{array}{l} \text{Cu} = 69 \cdot 6 \\ \text{Sn} = 30 \cdot 4 \end{array} \right\}$	Chill 1.	50 diameters.	Heat-oxidised.
5.	"	"	Chill 3.	50 "	" "
6.	"	"	Chill 5.	50 "	" "



4



5



6

the solidification of the whole mass to mixed crystals, which, assuming no lag in the transformations, should be uniform. The long slope OP would then correspond to the cooling of a solid mass of uniform crystals, and therefore the alloys chilled in this region of temperature show no pattern. But at P the solid solution becomes saturated, and on cooling below this point the band and fern leaf crystallises out. At a still lower temperature, probably Q, the mother substance of the fern leaf breaks up into a eutectic, formed in the solid. We think that P is a point on Austen and Stansfield's lower curve, and that Q is the eutectic angle of that curve. It will probably be found that the mother substance in all alloys from about B to D breaks up into a complex when the alloys cool to the temperature Q, so that if cooled slowly it is a eutectic, but if chilled above Q a homogeneous body.

It is not difficult to form a conception of how the type of pattern found below the temperature P originates. Slightly above the temperature O the alloy consisted of crystal grains surrounded by mother liquid somewhat richer in tin. At the moment of complete solidification the grains should have adjusted themselves so as to be identical throughout, but it is improbable that so perfect an equilibrium was attained, and the solid mass at temperatures below O must have contained nuclei richer in copper than the material surrounding them. In fact, prolonged polishing brings out a vague pattern in relief, showing differences of hardness, and therefore of composition. Now the alloy that we are considering lies to the right of Austen and Stansfield's eutectic angle in their lower curve; hence when the solid solution became saturated the new crystallisation commenced in the interspaces rich in tin, and more or less took their form. It is clear that the resulting structure would in section give the bands and polygons of the slow-cooled alloys. Similarly the inclusions of mother substance in the grains existing at O would be the origin of the isolated fern leaf.

Although it was hardly necessary, we thought it would be interesting to arrive at the condition of no pattern, starting from the solid alloy instead of from the liquid. We therefore took a fragment from an ingot of the same slowly cooled alloy, heated it to a faint red heat in the Bunsen flame, and dropped it into water. It showed no pattern after being polished and ignited to a pale orange. It was then heated to a temperature a little below redness, and allowed to cool for five minutes above the flame, repolished, and brought to the orange state. It then showed a very perfect slow-cooled pattern, the fern leaf being particularly good. The polygons appeared to be of the same size as in the original alloy, which had taken an hour or more to cool, but the bands were much thinner and the fern leaf smaller; the eutectic also was very scanty, while in the original ingot there were large spaces of

it. Thus the same alloy, without being melted, can by heating and chilling have all pattern removed, and by reheating, followed by a not very rapid cool, the pattern can be restored. The constancy in the size of the polygons points to their having been formed at an earlier period in the history of the alloy.

We see from the above that the patterns of slowly cooled copper-tin alloys are, at all events until they have been confirmed by the examination of chilled portions, entirely misleading as to the separations that occurred during solidification. Even the evidence for the existence of the compound  $\text{Cu}_3\text{Sn}$  will have to be revised; although in a somewhat altered form it will probably be found to be satisfactory.

We hope shortly to present to the Royal Society a more complete account of these alloys.

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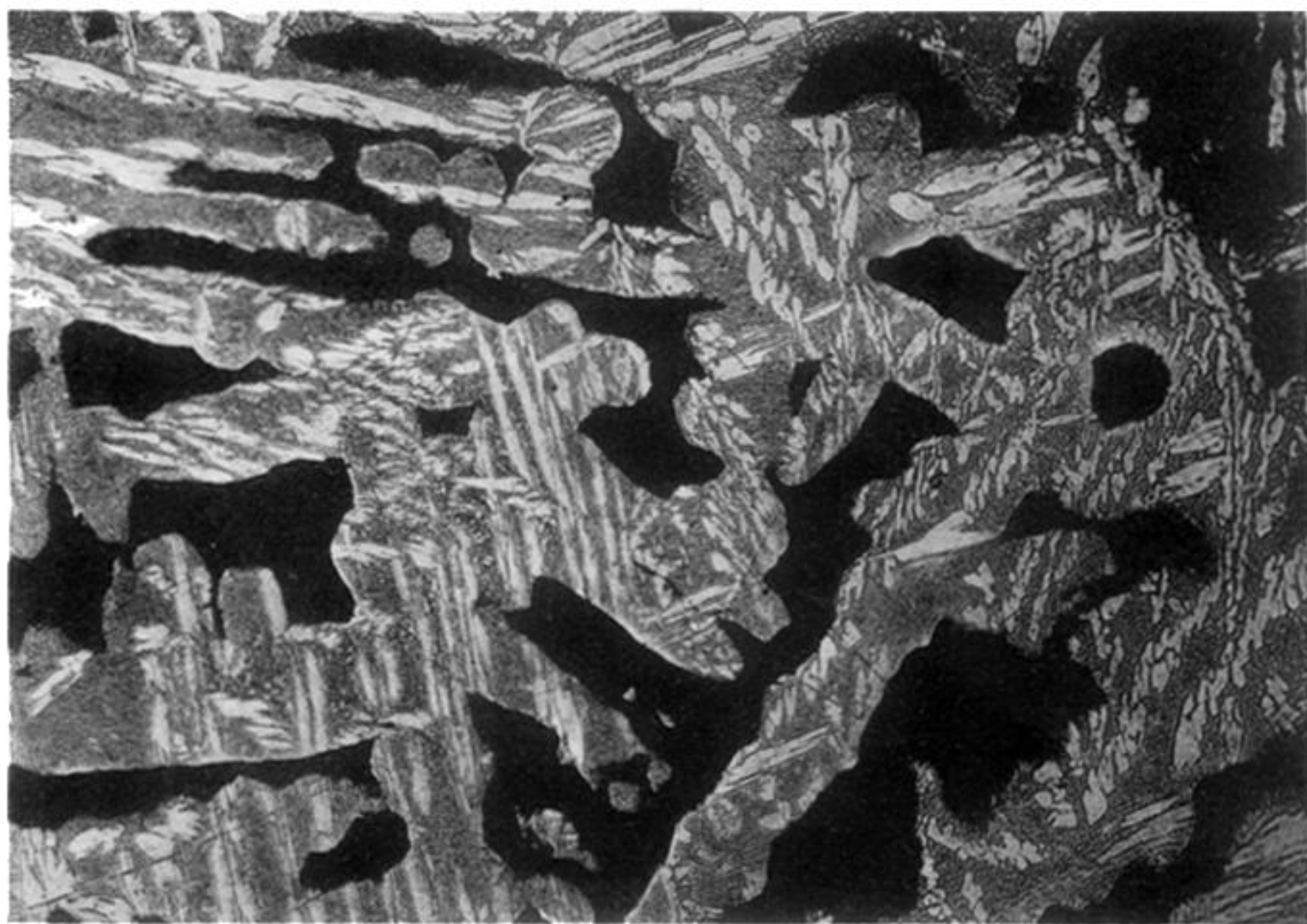
“On the Enhanced Lines in the Spectrum of the Chromosphere.” By Sir NORMAN LOCKYER, K.C.B., F.R.S., and F. E. BAXANDALL, A.R.C.S. Received March 19,—Read March 28, 1901.

In the recently published account\* of the spectroscopic results obtained by members of the expedition from the Yerkes Observatory, during the solar eclipse of May 28th, 1900, although the record of the wave-lengths of the lines photographed on the different eclipse plates is of great value, exception must be taken to the method of assigning origins to the lines. This question is so important just now that it is desirable to deal with it without delay. The only origins which Professor Frost appears to accept are those given by Rowland to any moderately strong solar line which agrees in position, either exactly or very nearly, with an eclipse line. In discussing the eclipse lines he has made specific allusions to the “enhanced” lines of some of the metals, and to their relationship—or non-relationship—to the eclipse lines.

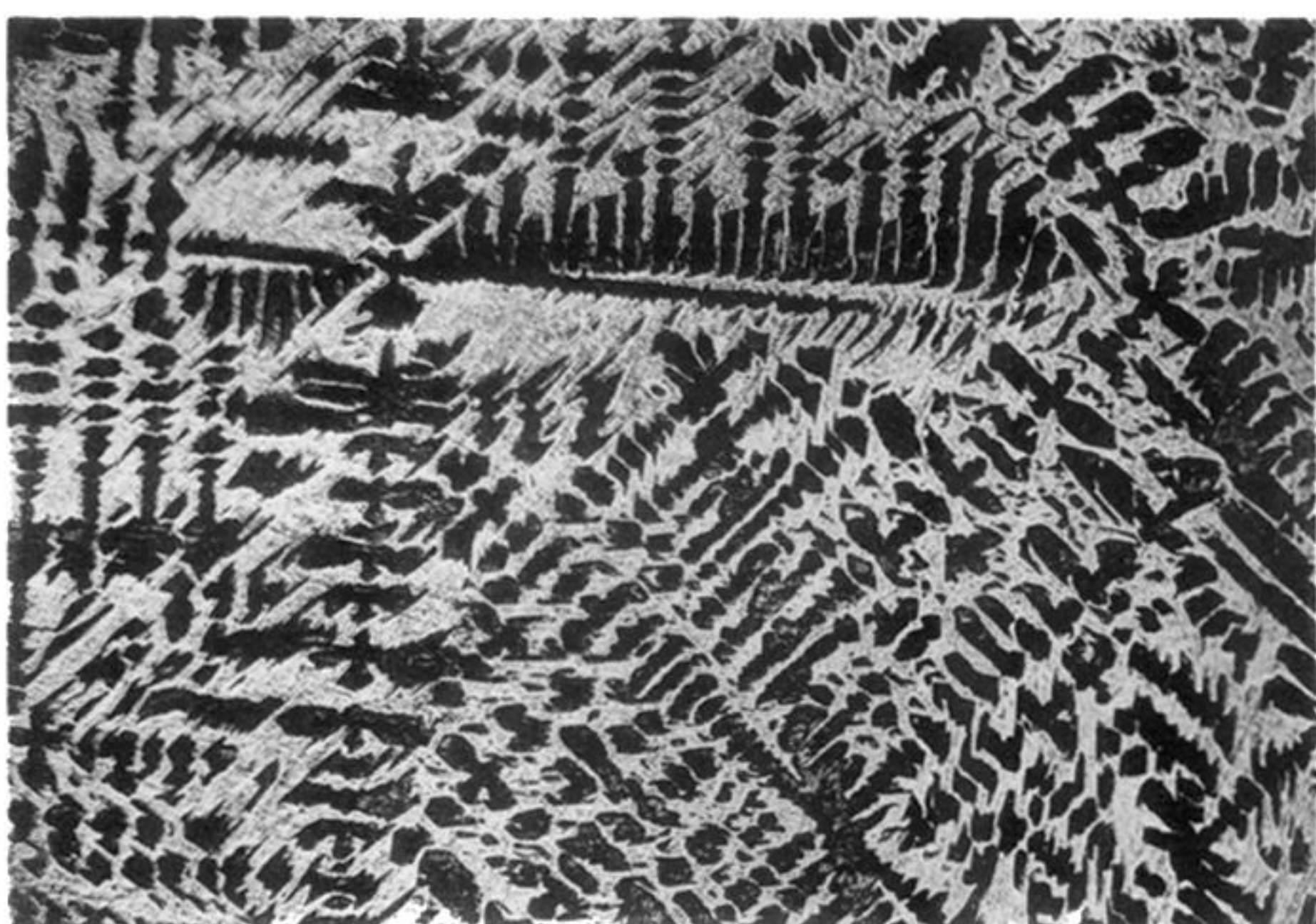
On p. 347 he says, “These plates give no evidence of any relationship between the bright lines and the ‘enhanced’ lines, or lines distinctly more intense in the spark than in the arc spectrum, although Sir Norman Lockyer has attached much significance to a supposed connection between them. Some of the enhanced lines are present and some are not, or at least were not conspicuous enough for measurement.” In the paragraph immediately following, he says, “In case of titanium, for which Lockyer gives 48 enhanced lines within our limits, we may summarise the comparison as follows: 17 lines do

\* Frost, ‘Ast.-Phys. Journ.,’ vol. 12, p. 307, 1900.

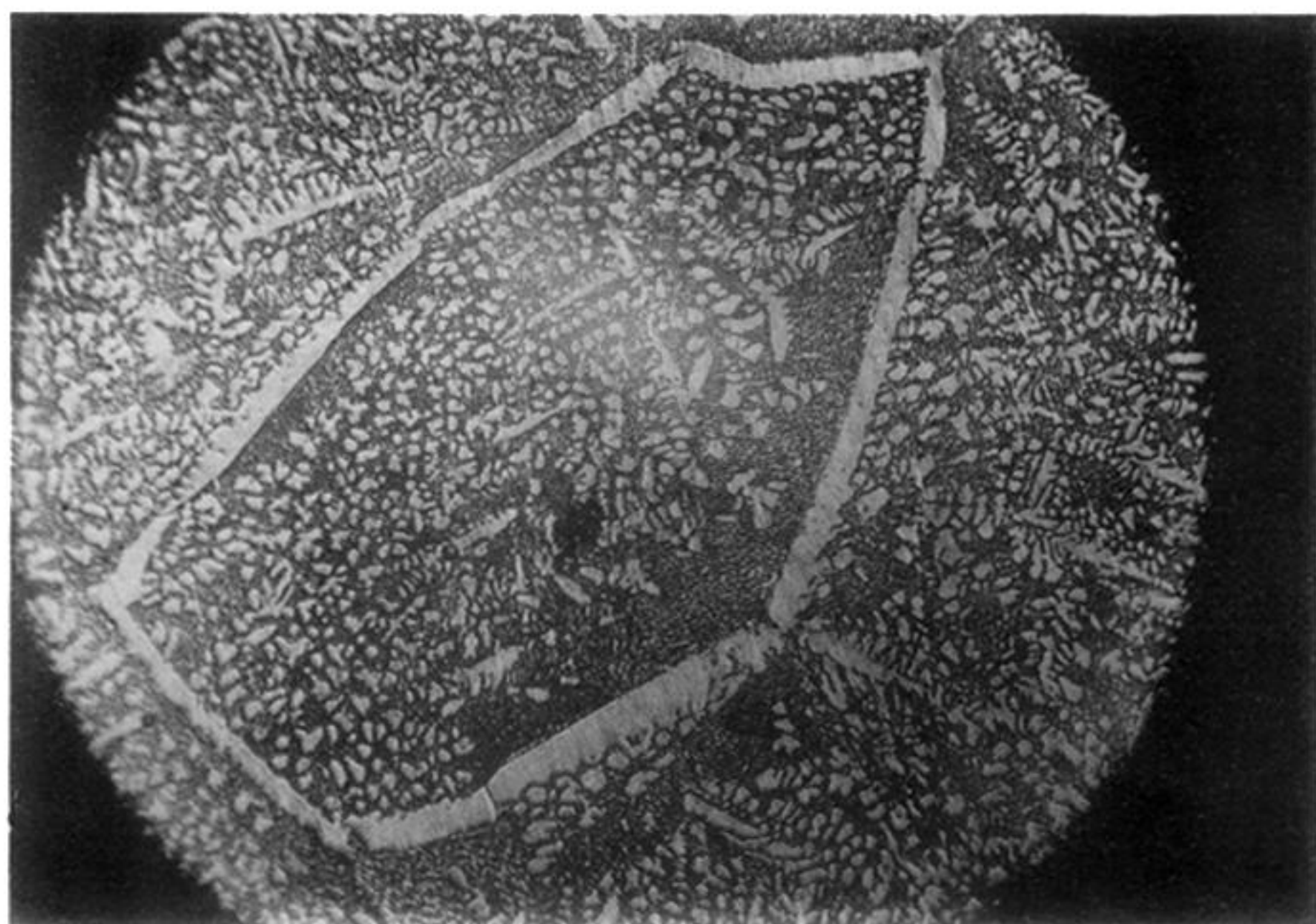




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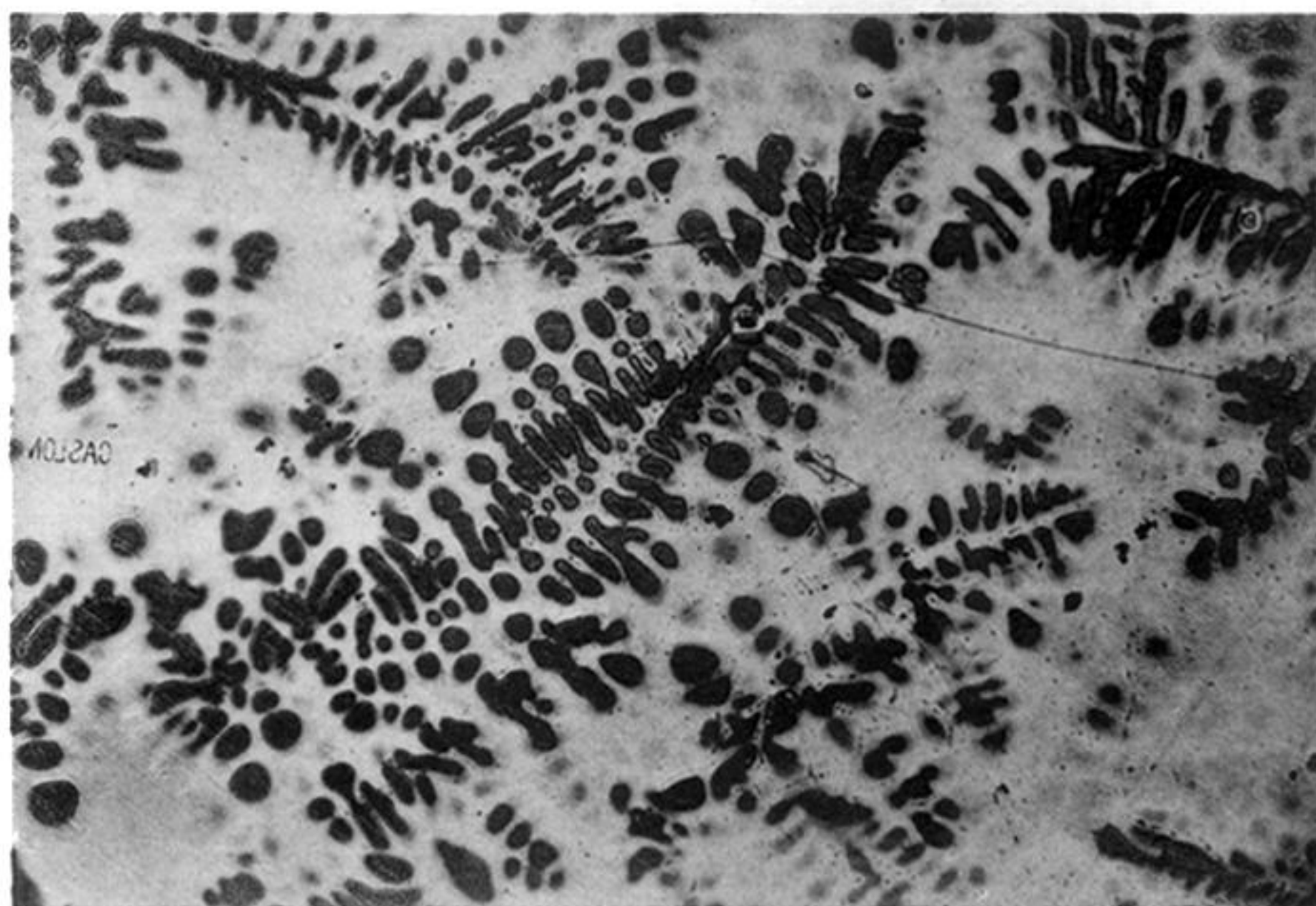
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## DESCRIPTION OF PLATE 2.

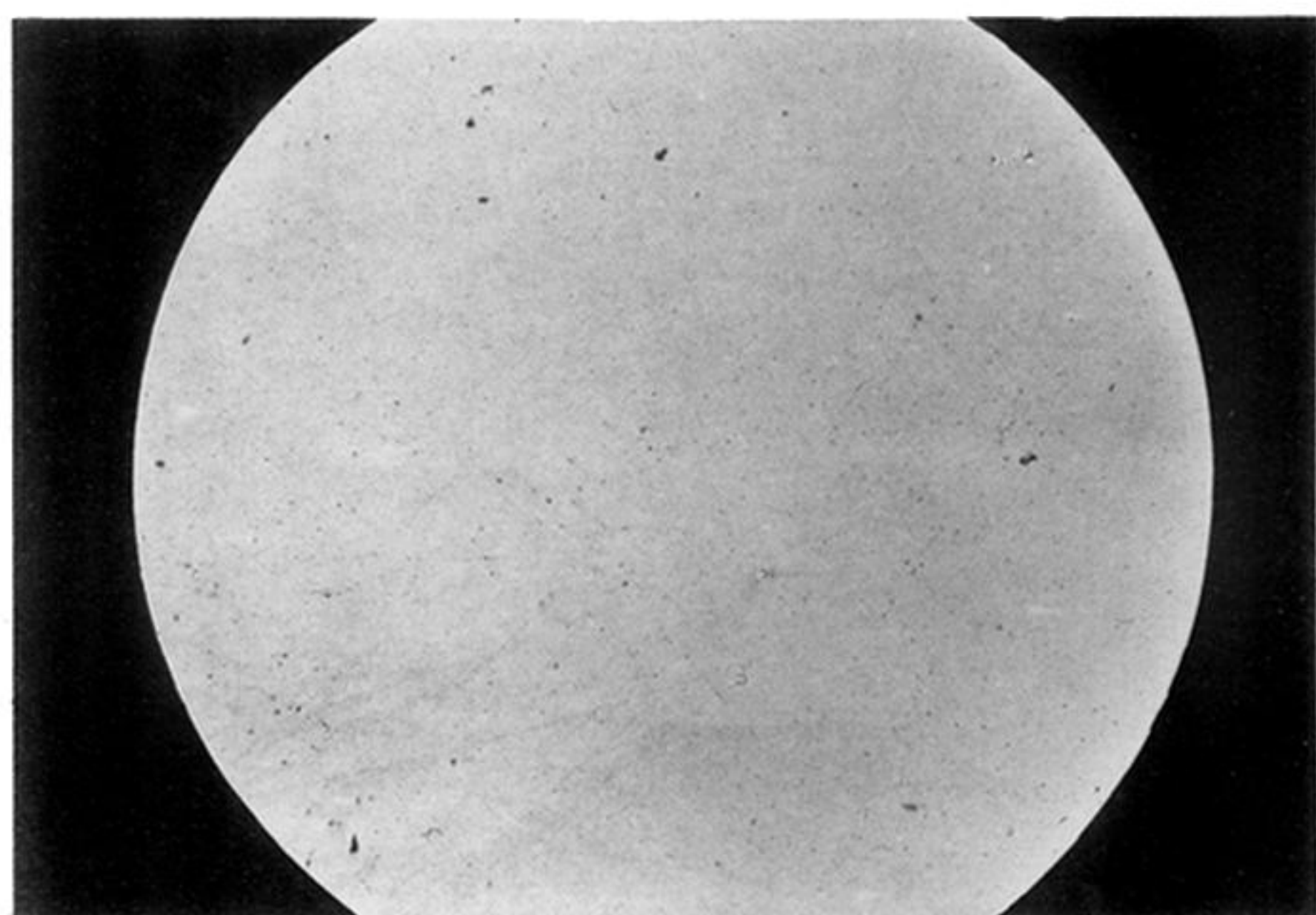
Slowly cooled alloys.

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3. $\text{Cu}_{83 \cdot 3}\text{Sn}_{16 \cdot 7}$	$\begin{cases} \text{Cu} = 72 \cdot 8. \\ \text{Sn} = 27 \cdot 2. \end{cases}$	300      „	„      „

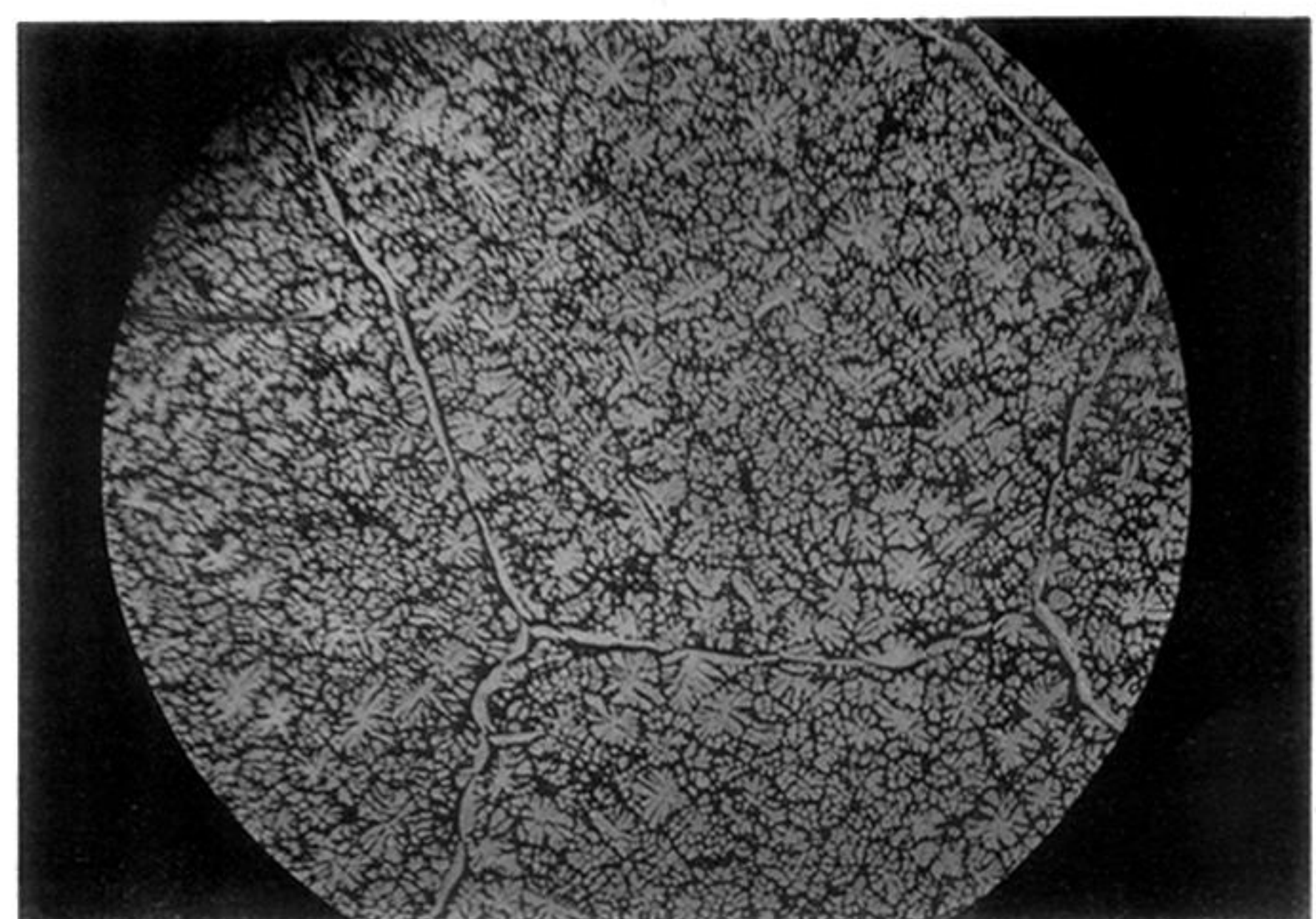




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### DESCRIPTION OF PLATE 3.

The same alloy chilled at different temperatures.

Formula	Percentage by weight.		Magnification.	Treatment.
4. $\text{Cu}_{81}\text{Sn}_{19}$	$\left\{ \begin{array}{l} \text{Cu} = 69.6 \\ \text{Sn} = 30.4 \end{array} \right\}$	Chill 1.	50 diameters.	Heat-oxidised.
5. "	"	Chill 3.	50 "	" "
6. "	"	Chill 5.	50 "	" "